

DEC 1951 51-48

25X1 [REDACTED]  
SECRET25X1 [REDACTED]  
CENTRAL INTELLIGENCE AGENCY**INFORMATION REPORT**

COUNTRY

USSR

SUBJECT

Soviet Research by Pudovik on New Reactions in Organophosphorous Compounds

25X1

25X1 PLACE ACQUIRED [REDACTED]

25X1 DATE ACQUIRED [REDACTED]

DATE (OF INFO.) [REDACTED]

25X1

DATE DISTR. 15 May 53

NO. OF PAGES 8

NO. OF ENCLS.

SUPP. TO  
REPORT NO.

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES. WITHIN THE MEANING OF TITLE 18, SECTIONS 793 AND 794, OF THE U.S. CODE, AS AMENDED. ITS TRANSMISSION OR REVELATION OF ITS CONTENTS TO OR RECEIPT BY AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. THE REPRODUCTION OF THIS REPORT IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

25X1

25X1

25X1

1. The following information is extracted from quite a large collection of material that became available only a short time ago (early 1953) and the entire stack of articles was published in one journal on the occasion of the seventy-fifth anniversary of Professor A E Arbuzov's birth. While each paper represents a legitimate continuation of the author's previous study of phosphorous compounds, [REDACTED] the following specific comments are warranted from the standpoints of interest and significance.

2. A N Pudovik of the A E Arbuzov Chemical Institute at Kazan and associates have published six recent articles on new reactions in organophosphorous compounds. The first two discuss a new reaction which is quite interesting from the viewpoint of chemists. While the work falls in line with Pudovik's earlier studies and while it is somewhat doubtful that the compounds he reports are of use as warfare agents, nevertheless any new substances such as these can conceivably be used as warfare agents, and are therefore worthy of noting even though their warfare use is only conjecture.

3. The next two articles are direct continuations of older work and there is better probability that the compounds described therein might be poisonous, although not on a scale that would make them war gasses or products.

4. The last two articles are legitimate continuations of previous work and have no particular significance.

- 25X1 5. For whatever it may be worth, [REDACTED] translated and digested these six articles as follows:

(a) New method of synthesis of esters of phosphonic and thiophosphonic acids.

Addition of dialkyl phosphites to unsaturated dibasic acids and esters, by A N

25X1 [REDACTED]  
SECRET

25X1 [REDACTED]

DISTRIBUTION	STATE	X	ARMY	X	NAVY	X	AIR		FBI		OSI/c	X		
--------------	-------	---	------	---	------	---	-----	--	-----	--	-------	---	--	--

25X1

SECRET

- 2 -

Pudovik of the A E Arbuzov Chem Inst at Kazan, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 926-31 (1952).

To 4.2 g maleic acid and 8 g  $(\text{MeO})_2\text{POH}$  was added some 10 drops of satd  $\text{MeONa}$  in abs  $\text{MeOH}$ , causing an exothermic reaction; distn gave 4.1 g  $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{PO}(\text{OMe})_2$ ,  $b_3 141^\circ$ ,  $n_D^{20} 1.4428$ ,  $d_4^{20} 1.2695$ , (50%). Similarly,  $(\text{EtO})_2\text{POH}$  with  $\text{EtONa-EtOH}$  catalyst gave 70.8% di-Et analog,  $b_1 137-8^\circ$ ,  $n_D^{20} 1.4408$ ,  $d_4^{20} 1.1782$ . Maleic anhydride (8 g) and 12 g  $(\text{MeO})_2\text{POH}$  heated on steam bath and treated dropwise with unstated amount of  $\text{MeONa-MeOH}$  also gave an exothermic reaction, however on attempted distn the product suffered decompn; similar result was encountered with  $(\text{EtO})_2\text{POH}$ . To 7.2 g di-Me maleate and 6 g  $(\text{MeO})_2\text{POH}$  was added 20 drops satd  $\text{MeONa-MeOH}$  with cooling (the temp rise to  $70^\circ$  was observed) and after 1 hr on a steam bath the mixture yielded 9.9 g (78%)  $\text{MeO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{Me})\text{PO}(\text{OMe})_2$ ,  $b_2 142^\circ$ ,  $n_D^{20} 1.4435$ ,  $d_4^{20} 1.2076$ . Similarly  $(\text{EtO})_2\text{POH}$  with  $\text{EtONa-EtOH}$  catalyst gave 81.9%  $\text{MeO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{Me})\text{PO}(\text{OEt})_2$  (I),  $b_{13} 184^\circ$ ,  $n_D^{20} 1.4422$ ,  $d_4^{20} 1.1803$ , while  $(\text{BuO})_2\text{POH}$  similarly gave the di-Bu ester analog, 69.7%,  $b_1 161-2^\circ$ ,  $n_D^{20} 1.4425$ ,  $d_4^{20} 1.0666$ . Heating 3.5 g I with 1:1  $\text{HCl}$  in sealed tube 6 hrs at  $120-300^\circ$  followed by evapn gave sirupy free acid. Reaction of 6.8 g di-Et fumarate with 6.5 g  $(\text{EtO})_2\text{POH}$  in presence of  $\text{EtONa-EtOH}$  gave 10.2 g (82.3%)  $\text{EtO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{Et})\text{PO}(\text{OEt})_2$ ,  $b_2 161-2^\circ$ ,  $n_D^{20} 1.4410$ ,  $d_4^{20} 1.1333$ ; similarly  $(\text{BuO})_2\text{POH}$  gave 95.7% di-Bu ester analog,  $b_2 178-9^\circ$ ,  $n_D^{20} 1.4417$ ,  $d_4^{20} 1.0673$ . Addn of few drops satd  $\text{EtONa-EtOH}$  to 5.6 g  $\text{EtO}_2\text{CC}(\text{CO}_2\text{Et})$  and 9.2 g  $(\text{EtO})_2\text{POH}$  caused no heat evolution, but continued addn caused a vigorous reaction; distn gave 6 g  $[\text{CH}(\text{CO}_2\text{Et})(\text{PO}(\text{OEt})_2)]_2$ , (II),  $b_5 213-14^\circ$ ,  $n_D^{20} 1.4700$ ,  $d_4^{20} 1.3753$ . Heating 7 g  $\text{EtO}_2\text{CC}(\text{CO}_2\text{Et})$ , 5.8 g  $(\text{EtO})_2\text{POH}$ , 20 ml  $\text{EtOH}$  and 1 ml satd  $\text{EtONa-EtOH}$  on steam bath 3 hrs gave 2.7 g II and 5 g product,  $b_8 125-85^\circ$ ; redista gave a fraction,  $b_3 160-3^\circ$ , contg 9.1% F, which indicated the addn of 1 mole  $(\text{EtO})_2\text{POH}$  to the triple link. Addn of M to 14 g  $\text{EtO}_2\text{CC}(\text{CO}_2\text{Et})$  and 9.5 g  $(\text{MeO})_2\text{POH}$  gave a vigorous reaction and distn of the mixture gave 3.2 g  $[\text{CH}(\text{CO}_2\text{Et})(\text{PO}(\text{OMe})_2)]_2$ ,  $b_3 200-3^\circ$ ,  $n_D^{20} 1.4635$ ,  $d_4^{20} 1.2715$ , and 15.6 g fraction,  $b_6 170-200^\circ$ , from which no individual substance could be fractionated. The structures of the diphosphonates listed above are not ascertained but appear probable.

(b) Addition of diethyl thiophosphite to ketones and aldehydes, by A N Pudovik and G A Zametaeva, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 932-9 (1952).

25X1

25X1

SECRET

- 3 -

In the presence of  $\text{EtONa}$ ,  $(\text{EtO})_2\text{PSH}$  forms an equilibrium mixture of  $\text{ROH}$  and  $(\text{RO})_2\text{P(S)Na}$ , which is capable of addn to various double bonds, including that of the carbonyl structures. Addn of 8 g  $(\text{EtO})_2\text{PSH}$  ( $b_p 63^\circ$ ,  $n_D^{20} 1.4587$ ,  $d_4^{20} 1.0763$ ) to 4.4 g ethylideneacetone, followed by dropwise addn of  $\text{EtONa-EtOH}$  led to vigorous reaction and distn of the mixture after 0.5 hr gave 6.2 g (50.1%)  $\text{AcCH}_2\text{CH=P(S)(OEt)}_2$ ,  $b_{12} 142-4^\circ$ ,  $n_D^{20} 1.4638$ ,  $d_4^{20} 1.0549$ , a greenish liquid with unpleasant odor. This (5 g) kept 5 days with 2.3 g  $\text{PhNHNH}_2$  and 6 ml abs  $\text{EtOH}$  in a desiccator, then distd gave 1.5 g corresponding phenylhydrazone,  $b_p 238-40^\circ$ , a red viscous liquid; the ester (1.5 g), 0.8 g semicarbazide-HCl in aq soln and 0.6 g  $\text{AcONa}$  treated with 5 ml  $\text{EtOH}$ , heated to boiling and cooled gave in 2-3 hrs the corresponding semicarbazone,  $m 124^\circ$  (from  $\text{EtOH}$ ). Addn of 15-20 drops  $\text{EtONa-EtOH}$  to 5.3 g  $(\text{EtO})_2\text{PSH}$  and 5 g benzalacetone similarly gave 4.6 g (46.5%)  $\text{AcCH}_2\text{CHPhP(S)(OEt)}_2$ ,  $b_p 177-3^\circ$ ,  $n_D^{20} 1.5344$ ,  $d_4^{20} 1.1462$ . Addn of 20 drops  $\text{EtONa-EtOH}$  to 6.85 g  $(\text{EtO})_2\text{PSH}$  and 5 g mesityl oxide, followed by 0.5 hr on a steam bath gave 8 g (74.1%)  $\text{AcCH}_2\text{C(Me)}_2\text{P(S)(OEt)}_2$ ,  $b_p 128-30^\circ$ ,  $n_D^{20} 1.4731$ ,  $d_4^{20} 1.0590$ ; phenylhydrazone,  $b_p 234-5^\circ$ , forms after 10 days at room temp with  $\text{PhNHNH}_2$  in  $\text{EtOH}$ ; semicarbazone,  $m 123^\circ$  (from  $\text{EtOH}$ ). Addn of 15 drops  $\text{EtONa-EtOH}$  to 5 g furfuralacetone and 6 g  $(\text{EtO})_2\text{PSH}$  similarly gave 5.1 g (48.7%) 1-furyl-1-(diethylthiophosphono)-3-butanone,  $b_p 164-6^\circ$ ,  $n_D^{20} 1.5025$ ,  $d_4^{20} 1.1471$ . Addn of 25-30 drops  $\text{EtONa-EtOH}$  to 17 g  $\text{Me}_2\text{CO}$  and 4.8 g  $(\text{EtO})_2\text{PSH}$  caused but a mild reaction; after 2 hrs on a steam bath the mixture yielded 4 g (62.1%)  $\text{Me}_2\text{C(OH)P(S)(OEt)}_2$ ,  $b_{10} 107-9^\circ$ ,  $n_D^{20} 1.4684$ ,  $d_4^{20} 1.0735$ , whose  $\text{EO}$  group is determinable by Zerevitinov method. Addn of 20 drops  $\text{EtONa-EtOH}$  to 10 g  $(\text{EtO})_2\text{PSH}$  and 3.6 g acrolein stabilized with hydroquinone, with cooling, followed by neutralization with  $\text{AcOH}$  and distn, gave 6 g (45.2%)  $\text{CH}_2=\text{CHCH(OH)P(S)(OEt)}_2$ ,  $b_{10} 120-2^\circ$ ,  $n_D^{20} 1.4828$ ,  $d_4^{20} 1.1156$ ;  $\text{PhNHNH}_2$  in  $\text{EtOH}$  in 6 days gave no phenylhydrazone, and a similar neg result was secured with semicarbazide; quant bromination showed 1 double bond.  $\text{EtONa-EtOH}$  added to 4.4 g  $(\text{EtO})_2\text{PSH}$  and 2 g crotonaldehyde gave a vigorous reaction and distn of the product gave 2.4 g (43.7%)  $\text{MeCH=CHCH(OH)P(S)(OEt)}_2$ ,  $b_p 130-2^\circ$ ,  $n_D^{20} 1.4846$ ,  $d_4^{20} 1.1019$ . To 4 g  $(\text{EtO})_2\text{PSH}$  and 3.2 g furylacrolein in 6 ml abs  $\text{EtOH}$  was added  $\text{EtONa-EtOH}$ ; the reaction was less vigorous than the preceding one; distn gave 2.8 g (46.1%) 1-hydroxy-3-furyl-1-(diethylthiophosphono)-2-propene,  $b_{10} 101-2^\circ$ ,  $n_D^{20} 1.5280$ ,  $d_4^{20} 1.0785$ ,  $m 25-6^\circ$ . Addn of 20 drops  $\text{EtONa-EtOH}$  to 5 g  $(\text{EtO})_2\text{PSH}$  and 1.5 g  $\text{AcH}$  gave a vigorous reaction and

SECRET

25X1

25X1

SECRET

25X1

- 4 -

after 24 hrs at room temp the mixture gave 4.6 (62.3%)  $\text{MeCH}(\text{OEt})\text{P}(\text{S})(\text{OEt})_2$ ,  $b_{12} 111-12^\circ$ ,  $n_D^{20} 1.4721$ ,  $d_4^{20} 1.1029$ . Similar reaction with  $\text{PhCHO}$  gave 45.4%  $\text{PhCH}(\text{OEt})\text{P}(\text{S})(\text{OEt})_2$ ,  $b_{12} 122-3^\circ$ ,  $n_D^{20} 1.4781$ ,  $d_4^{20} 1.0925$ .

(c) New method of synthesis of esters of aminophosphonic acids, by A N Pudovik and M V Korchemkina, published in Izvest Akad Nauk SSSR, Otdel. Khim Nauk 940-6 (1952).

$(\text{RO})_2\text{POH}$  add to derivs of benzalaniline in the presence of  $\text{LiNa}$  catalyst yielding esters of aminophosphonic acids in good yields. To avoid ester exchange the  $\text{RONa}$  must have the same radical R as the dialkyl phosphite. The general procedure of addn of 15-20 drops satd  $\text{RONa-ROH}$  to 3-4 g benzalaniline deriv and equimolar amount of  $(\text{RO})_2\text{POH}$ , followed by one hour on a steam bath gave the products in crystalline form after several hours or days standing in an open dish; crystallization from  $\text{EtOH}$  gave the pure products listed below. With acetophenoneanil it was necessary to heat the mixture 1-2 hours at  $150-80^\circ$  to complete the reaction. The following esters were reported. p-iso- $\text{PrC}_6\text{H}_4\text{CH}(\text{NHPh})\text{PO}(\text{OMe})_2$ , 67.7%, m  $106-7^\circ$ ; di-Et analog, 76.6%, m  $150^\circ$ ; p-MeC<sub>6</sub>H<sub>4</sub>CH(NHPh)PO(OMe)<sub>2</sub>, 77.8%, m  $121-2^\circ$ ; di-Et analog, 82.3%, m  $66^\circ$ ; o-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(NHPh)PO(OMe)<sub>2</sub>, 77.2%, m  $175.5-6.0^\circ$ ; di-Et analog, 87.7%, m  $155^\circ$ ; m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(NHPh)PO(OMe)<sub>2</sub>, 82.8%, m  $130-1^\circ$ ; di-Et analog, 90.9%, m  $93-4^\circ$ ; PhCH(PO(OEt)<sub>2</sub>)NHC<sub>6</sub>H<sub>4</sub>Cl-p, 75.4%, m  $111-13^\circ$ ; m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(PO(OEt)<sub>2</sub>)NHC<sub>6</sub>H<sub>4</sub>Me-m, 78.7%, m  $129-30^\circ$ ; p-iso- $\text{PrC}_6\text{H}_4\text{CH}(\text{PO}(\text{OEt})_2)\text{NHC}_6\text{H}_4\text{Cl-p}$ , 82.7%, m  $119-9.5^\circ$ ; p-MeC<sub>6</sub>H<sub>4</sub>CH(PO(OEt)<sub>2</sub>)NHC<sub>6</sub>H<sub>4</sub>Me-m, 88%, m  $102-3^\circ$ ; p-iso- $\text{Pr-C}_6\text{H}_4\text{CH}(\text{PO}(\text{OEt})_2)\text{NHC}_6\text{H}_4\text{Me-o}$ , 79.1%, m  $115^\circ$ ; MeEtC(NHPh)PO(OEt)<sub>2</sub>, 75%, m  $106-8^\circ$ ; Et<sub>2</sub>C(NHPh)PO(OEt)<sub>2</sub>, 78.8%, m  $119-20^\circ$ . Reaction products with  $(\text{RO})_2\text{POH}$  and o-hydroxybenzalaniline failed to crystallize; the reaction apparently failed to take place with benzo-phenoneanil, acetophenone-o-methylanil and the m-analog; at least, no crystalline products could be obtained. Reaction of  $(\text{EtO})_2\text{POH}$  with benzalaniline was investigated in 0.725-1.45 M solns in the presence of 17.4% MeONa in MeOH at  $70^\circ$ ; the titration of unreacted  $(\text{EtO})_2\text{POH}$  with 0.5N NaOH in presence of phenolphthalein was used as the means of following the reaction. In abs EtOH the reaction failed to occur at low concns, while at high concns it ran its course too rapidly and with too much heat evolution for accurate detns of the rate. These results were obtained with EtOH dried over CaO, followed by Na. Use of EtOH that was additionally dried over Mg gave much better results. At  $50^\circ$  a

25X1

SECRET

25X1

SECRET

25X1

25X1

- 5 -

1.45 M soln of the reagents (50 ml) with 0.5 ml MeONa soln added gave a straight line decrease of unreacted  $(\text{EtO})_2\text{POH}$  with some 25% completion in six hours; with 1 ml catalyst the reaction was 50% complete almost instantly after which it followed a logarithmic curve approaching 90% at six hours; with 3 ml catalyst the reaction was nearly instantaneous; with 0.725M soln at  $30.4^\circ$  the results are similar, very little reaction taking place with 2 ml catalyst, some 90% completion with 2.5 ml and instantaneous reaction with 3 ml. The results indicate extraordinary sensitivity of the reaction to traces of moisture, which destroys  $(\text{EtO})_2\text{PONA}$ ; this confirms the ionic chain mechanism of the addn reaction.

(d) Addition of dialkyl phosphites and their chlorides to  $\alpha$ -oxides, by A N Pudovik and B E Ivanov of the Kazan State University, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 947-55 (1952).

Passage of ethylene oxide (I) into  $\text{Et}_2\text{O}$  soln of  $(\text{EtO})_2\text{PONA}$ , treatment with AcOH, filtration and distn gave largely the original ester and only a trace of product,  $b_{115-25}^\circ$ , along with much tar. Run at elevated temp the reaction gives but slightly improved yields.  $\text{BF}_3$  and its adducts are the best catalysts for addn of dialkyl phosphites to olefin oxides. Heating 20 g  $(\text{EtO})_2\text{POH}$ , 10 g I and 0.015 ml  $\text{BF}_3\text{-Et}_2\text{O}$  in a sealed tube eight hours at  $130^\circ$  gave after two distns 3.5 g  $\text{HOCH}_2\text{CH}_2\text{PO}(\text{OEt})_2$ ,  $b_{122-4}^\circ$ ,  $n_D^{20} 1.4380$ ,  $d_4^{20} 1.0927$ ; at lower temp the reaction is very slow, at higher temp much destruction of the products occurs. Small amounts of concd  $\text{H}_2\text{SO}_4$  give somewhat lower yields than does  $\text{BF}_3$ . Heating 20 g  $(\text{MeO})_2\text{POH}$  with 12 g I and 0.015 ml  $\text{BF}_3\text{-Et}_2\text{O}$  eight hours at  $130-5^\circ$  in sealed tube gave 3 g  $\text{HOCH}_2\text{CH}_2\text{PO}(\text{OMe})_2$ ,  $b_{95-7}^\circ$ ,  $n_D^{20} 1.4240$ ,  $d_4^{20} 1.1711$ .  $(\text{iso-BuO})_2\text{POH}$  (15 g) and 7 g I with 0.015 ml  $\text{Et}_2\text{O-BF}_3$  failed to react even at  $160-70^\circ$ ; the di-Bu ester also gave negative results at  $135^\circ$ . To soln of 2.3 g Na in 13.8 g  $(\text{EtO})_2\text{POH}$  in 100 ml  $\text{Et}_2\text{O}$  was added 10.2 g  $\text{EtOCH}_2\text{CHCH}_2\text{O}$ , the mixture was refluxed wree hours, treated with 7 ml AcOH, filtered, and distd yielding 3.5 g crude, or 1.7 g pure,  $\text{EtOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{PO}(\text{OEt})_2$ ,  $b_{115-16}^\circ$ ,  $d_4^{20} 1.0831$ ,  $n_D^{20} 1.4385$ . Reaction of 13.8 g  $(\text{EtO})_2\text{POH}$  with 10.2 g  $\text{EtOCH}_2\text{CHCH}_2\text{O}$  and 0.05 ml  $\text{BF}_3\text{-Et}_2\text{O}$  in eight hours at  $130-5^\circ$  in sealed tube gave 3 g product,  $b_{137-9}^\circ$ ,  $d_4^{20} 1.1023$ ,  $n_D^{20} 1.4432$ , and 2.5 g product,  $b_{155-6}^\circ$ ,  $n_D^{20} 1.4520$ .

25X1

SECRET

25X1

SECRET

25X1

- 6 -

$d_4^{20}$  1.1745; the former contained 13%P, the latter 15%P; it is believed that with  $\text{BF}_3$  catalyst the reaction yields as one product di-Et  $\beta$ -hydroxy- $\beta$ -ethoxyisopropylphosphonate. Heating 25 g  $(\text{EtO})_2\text{POH}$  with 16 g cyclohexene oxide and 0.015 ml  $\text{BF}_3\text{-Et}_2\text{O}$  in ampul eight hours at  $140-50^\circ$  gave 4.5 g di-Et  $\beta$ -hydroxy-cyclohexylphosphonate,  $\text{C}_{10}\text{H}_{21}\text{O}_4\text{P}$ ,  $b_8$  142-4 $^\circ$ ,  $d_4^{20}$  1.0930,  $n_D^{20}$  1.4620. Passage of I into 35 g  $(\text{EtO})_2\text{PCl}$  until 10 g wt gain was reached at  $20-5^\circ$ , followed by distn gave: 4 g  $(\text{EtO})_3\text{P}$ ,  $b_7$  46 $^\circ$ ,  $n_D^{20}$  1.4138,  $d_4^{20}$  0.9866; 20 g  $(\text{EtO})_2\text{POCH}_2\text{CH}_2\text{Cl}$ ,  $b_5$  72-4 $^\circ$ ,  $n_D^{20}$  1.4392,  $d_4^{20}$  1.1038; and 8 g  $\text{EtOP}(\text{OCH}_2\text{CH}_2\text{Cl})_2$ ,  $b_{15}$  125-8 $^\circ$ ,  $n_D^{20}$  1.4609,  $d_4^{20}$  1.2268. Heating 10 g II with 5.5 g  $\text{EtBr}$  in sealed tube five hours at  $-160^\circ$  gave 7 g  $\text{EtPO}(\text{OEt})(\text{OCH}_2\text{CH}_2\text{Cl})$ ,  $b_7$  67-8 $^\circ$ ,  $d_4^{20}$  1.0911,  $n_D^{20}$  1.4168. Addn of 10 g  $(\text{EtO})_2\text{PCl}$  to  $\text{Et}_2\text{O}$  soln of  $\text{MeCHMeCHMeO}$  (unstated amount) with cooling gave 2.5 g  $(\text{EtO})_3\text{P}$ , and 5 g (55%)  $(\text{EtO})_2\text{POCHMeCHMeCl}$ ,  $b_{12}$  99 $^\circ$ ,  $n_D^{20}$  1.4367,  $d_4^{20}$  1.0633, and 4 g  $\text{EtOP}(\text{OCHMeCHMeCl})_2$ ,  $b_5$  130-2 $^\circ$ ,  $n_D^{20}$  1.4500,  $d_4^{20}$  1.0931. Addn of 6.5 g  $(\text{EtO})_2\text{PCl}$  to 4 g cyclohexene oxide gave an exothermic reaction and on distn there was obtained after two fractionations 3 g diethyl 2-chloro-cyclohexyl phosphite,  $b_{17}$  130-2 $^\circ$ ,  $n_D^{20}$  1.4650,  $d_4^{20}$  1.1082. Passage of I (5:5 g weight gain) into 15 g  $\text{CH}_2\text{CH}_2\text{OPClO}$  with cooling gave on distn 19 g  $\text{CH}_2\text{CH}_2\text{OP}(\text{OCH}_2\text{CH}_2\text{Cl})\text{O}$ ,  $b_{10}$  82-3 $^\circ$ ,  $d_4^{20}$  1.3185,  $n_D^{20}$  1.4760.

(e) Reaction of phosphonocethylation and diene synthesis with vinylphosphonic esters, by A N Pudovik and M G Imaev of the Kazan State University, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 916-22 (1952).

Attempts to obtain  $\text{BrCH}_2\text{CH}_2\text{P}(\text{O})(\text{OMe})_2$  from  $(\text{MeO})_3\text{P}$  and  $(\text{CH}_2\text{Br})_2$  failed since the  $\text{MeBr}$  evolved caused immediate isomerization of  $(\text{MeO})_3\text{P}$ . However, when 150 g  $(\text{CH}_2\text{Br})_2$  was added dropwise to 30 g  $(\text{BuO})_3\text{P}$  preheated to  $170^\circ$  and heated 3.5 hrs at  $170-90^\circ$  with evolution of  $\text{BuBr}$  there was obtained 2 g  $\text{BuP}(\text{O})(\text{OBu})_2$  and 19.8 g  $\text{BrCH}_2\text{CH}_2\text{P}(\text{O})(\text{OBu})_2$ , contaminated with some of the previous ester; this product  $b_5$  146-7 $^\circ$ ,  $n_D^{20}$  1.4485,  $d_4^{20}$  1.1400; also was obtained 2.5 g  $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OBu})_2$ ,  $b_7$  207-10 $^\circ$ ,  $n_D^{20}$  1.4402,  $d_4^{20}$  1.0240. If the order of addn is reversed the reaction failed to take place owing to too low b pt of  $(\text{CH}_2\text{Br})_2$ . To 15 g  $\text{Br}$  deriv in 100 ml  $\text{EtOH}$  was added dropwise 2.5 g  $\text{KOH}$  in  $\text{EtOH}$  with ice-cooling; distn after filtration gave 7 g  $\text{CH}_2\text{:CHP}(\text{O})(\text{OBu})_2$ ,  $b_5$  115-6 $^\circ$ ,  $n_D^{20}$  1.4372,  $d_4^{20}$  0.9810, (75%), (I). Heating 40.5 g  $(\text{MeO})_3\text{P}$  with 100 g  $(\text{CH}_2\text{Br})_2$  to  $150^\circ$

25X1

SECRET

25X1

SECRET

25X1

- 7 -

gave much MeBr (10 g) and distn gave 50 g  $(CH_2Br)_2$ , 15 g  $(MeO)_3P$  and 25 g  $MeP(O)-(OMe)_2$ ,  $b_p 66-8^\circ$ ,  $n_D^{20} 1.4135$ ,  $d_4^{20} 1.1684$ , as well as some tarry material. To 6 g  $CH_2:CHP(O)(OEt)_2$ , (II), in 42 g abs EtOH and 0.3 g EtONa, was added  $H_2S$  until the soln was satd at room temp; after 24 hrs distn gave 3 g unreacted II and 2.5 g  $HSCH_2CH_2P(O)(OEt)_2$ ,  $b_p 95-6^\circ$ ,  $n_D^{20} 1.4210$ ,  $d_4^{20} 1.0392$ ; 75% yield is achieved if the reaction is run at  $100^\circ$  in sealed tube 15 hrs. Heating 5 g II with 4 g EtSH and 0.3 g EtONa in sealed tube 18 hrs at  $100^\circ$  gave 3.5 g  $EtSCH_2CH_2P(O)(OEt)_2$ ,  $b_p 96^\circ$ ,  $n_D^{20} 1.4265$ ,  $d_4^{20} 1.0406$ . Heating 5 g I with 4.5 g EtSH and a little BuONa in sealed tube at  $100^\circ$  gave 3.1 g  $EtSCH_2CH_2P(O)(OBu)_2$ ,  $b_p 165-7^\circ$ ,  $n_D^{20} 1.4580$ ,  $d_4^{20} 1.0109$  (78%). Heating 7 g II, 10 g piperylene and 0.1 g hydroquinone in sealed tube 25 hrs at  $170-80^\circ$  gave 3 g piperylene dimer, 2.5 g II and 3.5 g, 63.5% d1-Et 2-methyl- $\Delta^3$ -cyclo-hexenephosphonate,  $b_p 118-19^\circ$ ,  $n_D^{20} 1.4488$ ,  $d_4^{20} 1.0166$ . Similar reaction with I at  $190-200^\circ$  gave 65.2% d1-Bu ester analog,  $b_p 155-6^\circ$ ,  $n_D^{20} 1.4801$ ,  $d_4^{20} 1.0379$ . Heating 3 g II and 10 g 2,4-hexadiene with a little hydroquinone in sealed tube 25 hrs at  $250-70^\circ$  gave 2 g (44%) d1-Et 2,5-dimethyl- $\Delta^3$ -cyclohexenephosphonate,  $b_p 125-7^\circ$ ,  $n_D^{20} 1.4505$ . Similar reaction with I at  $270-90^\circ$  gave 36.4% d1-Bu ester analog,  $b_p 154-6^\circ$ ,  $n_D^{20} 1.4710$ ,  $d_4^{20} 1.0042$ . The reaction products from piperylene were single substances, indicating that the addn occurs in accord with the electronic theory with development of neg center at the terminal C atom of piperylene and pos center at the terminal atom of I or II.

(f) New method of synthesis of esters of phosphonic and thiophosphonic acids, 5, Addition of esters of phenyl- and alkylphosphonous acids to esters of methacrylic and acrylic acids, by A N Pud'evik and D Kh Yarmukhametova of the A E Arbuzov Chem Institute at Kazan, published in Izvest Akad Nauk SSSR, Otdel Khim Nauk, 902-7 (1952).

To 15 g abs MeOH was gradually added 14.6 g  $PhPCl_2$ , the resulting HCl was removed in vacuo over 3-4 hrs and the residue on distn gave 8.4 g (66%)  $PhP(OMe)OH$ ,  $b_p 91-3^\circ$ ,  $n_D^{20} 1.5322$ ,  $d_4^{20} 1.1770$ .  $PhPCl_2$  (25 g) and 20 g abs EtOH gave 20 g (84%)  $PhP(OEt)OH$ ,  $b_p 94-5^\circ$ ,  $n_D^{20} 1.5231$ ,  $d_4^{20} 1.1291$ .  $PhPCl_2$  (11.3 g) and 11.3 g abs iso-PrOH gave 70%  $PhP(OCHMe_2)OH$ ,  $b_p 106-7^\circ$ ,  $n_D^{20} 1.5111$ ,  $d_4^{20} 1.0922$ ; similarly 14.8 g  $PhPCl_2$  and 18.5 g iso-BuOH gave 88%  $PhP(OCH_2CHMe_2)OH$ ,  $b_p 112-13^\circ$ ,  $n_D^{20} 1.5081$ ,  $d_4^{20} 1.0675$ ; 10.7 g  $PhPCl_2$  and 18.3 g  $C_6H_{13}OH$  gave 60%  $PhP(OC_6H_{13})OH$ ;  $b_p 139^\circ$ ,

25X1

SECRET

25X1

SECRET

25X1

- 8 -

$n_D^{20}$  1.5030,  $d_4^{20}$  1.0388; 10 g  $\text{PhPCl}_2$  and 19 g  $\text{C}_7\text{H}_{15}\text{OH}$  gave 80%  $\text{PhP}(\text{OC}_7\text{H}_{15})\text{OH}$ ,  $b_{150}^\circ$ ,  $n_D^{20}$  1.4996,  $d_4^{20}$  1.0187; 8.8 g  $\text{PhPCl}_2$  and 19.2 g  $\text{C}_8\text{H}_{17}\text{OH}$  gave 78%  $\text{PhP}(\text{OC}_8\text{H}_{17})\text{OH}$ ,  $b_{155}^\circ$ ,  $n_D^{20}$  1.4982,  $d_4^{20}$  1.0079; 10 g  $\text{PhPCl}_2$  and 24 g  $\text{C}_9\text{H}_{19}\text{OH}$  gave 57%  $\text{PhP}(\text{OC}_9\text{H}_{19})\text{OH}$ ,  $b_{158-60}^\circ$ ,  $n_D^{20}$  1.4900,  $d_4^{20}$  0.9843. Addn of these esters to acrylates and methacrylates gave products with sharp b pts without any evidence of ester exchange, even when  $\text{EtONa}$  was used as catalyst. Thus, to 7 g  $\text{PhP}(\text{OEt})\text{OH}$  and 4.1 g  $\text{CH}_2=\text{CMe}-\text{CO}_2\text{Me}$  was added 4-5 drops satd  $\text{EtOH}-\text{EtONa}$  and after the exothermic reaction the mixture gave on distn 8 g  $\text{MeO}_2\text{CCHMeCH}_2\text{P}(\text{Ph})(\text{O})\text{OEt}$ ,  $b_{151-52}^\circ$ ,  $n_D^{20}$  1.5064,  $d_4^{20}$  1.1390, 72%. Similarly  $\text{CH}_2=\text{CHCO}_2\text{Me}$  gave 76%  $\text{MeO}_2\text{CCH}_2\text{CH}_2\text{P}(\text{Ph})(\text{O})\text{OEt}$ ,  $b_{159-60}^\circ$ ,  $n_D^{20}$  1.5081,  $d_4^{20}$  1.1619; use of  $\text{CH}_2=\text{CMeCO}_2\text{Et}$  gave 82%  $\text{EtO}_2\text{CCHMeCH}_2\text{P}(\text{Ph})(\text{O})\text{OEt}$ ,  $b_{159-60}^\circ$ ,  $n_D^{20}$  1.4992,  $d_4^{20}$  1.1140; use of  $\text{CH}_2=\text{CMeCO}_2\text{Pr}$  gave 74%  $\text{PrO}_2\text{CCHMeCH}_2\text{P}(\text{Ph})(\text{O})\text{OEt}$ ,  $b_{159-60}^\circ$ ,  $n_D^{20}$  1.4962,  $d_4^{20}$  1.0988. Similarly, 6.1 g  $\text{PhP}(\text{OCH}_2\text{CHMe}_2)\text{OH}$  and 3 g  $\text{CH}_2=\text{CMeCO}_2\text{Me}$  gave 45%  $\text{MeO}_2\text{CCHMeCH}_2\text{P}(\text{Ph})(\text{O})\text{CH}_2\text{CHMe}_2$ ,  $b_{156}^\circ$ ,  $n_D^{20}$  1.4965,  $d_4^{20}$  1.0962; similarly was obtained 40%  $\text{MeO}_2\text{CCHMeCH}_2\text{P}(\text{Ph})(\text{O})\text{OC}_6\text{H}_{13}$ ,  $b_{176-7}^\circ$ ,  $n_D^{20}$  1.4908,  $d_4^{20}$  1.0589. Reactions of  $\text{RP}(\text{OR})\text{OH}$ , where R = alkyl group with unsatd esters gave mixtures with wide b pts unless the R of  $\text{RONa}$  catalyst was identical with the R of the esters used. With this precaution, 4 g  $\text{EtP}(\text{OBu})\text{OH}$  and 3.8 g  $\text{CH}_2=\text{CMeCO}_2\text{Bu}$  gave 77%  $\text{BuO}_2\text{CCHMeCH}_2\text{P}(\text{Et})(\text{O})\text{OBu}$ ,  $b_{137-8}^\circ$ ,  $n_D^{20}$  1.4490,  $d_4^{20}$  1.0025, while  $\text{CH}_2=\text{CHCO}_2\text{Bu}$  gave 74%  $\text{BuO}_2\text{CCH}_2\text{CH}_2\text{P}(\text{Et})(\text{O})\text{OBu}$ ,  $b_{141}^\circ$ ,  $n_D^{20}$  1.4490,  $d_4^{20}$  1.0146. In all esters of type  $\text{PhP}(\text{OR})\text{OH}$  the found value of molecular refraction exceeded the calcd values by 1.1-1.5 units indicating a constitutive effect of Ph group on refractivity of P.

- end -

25X1

SECRET



25X1



*Missing*

*6/28/65*